

Alkyl Derivatives and Oxidation Products

OF SOME

QUINOLINE BASES

AND OVER

Triphenyl-methyl-arsonium oxide.

INAUGURAL DISSERTATION

APPLYING FOR THE DEGREE

OF

DOCTOR OF PHILOSOPHY

TO THE

PHILOSOPHICAL FACULTY

OF THE

ROSTOCK UNIVERSITY

PRESENTED BY

VICKERS OBERHOLTZER

FROM

PHILADELPHIA.

U. S. A.

1895

REFERENT :

HERRN. PROFESSOR DR. MICHAELIS.



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INTRODUCTION.

Although many Quinoline derivatives have already been made, the work is as yet by no means complete. At the instigation of my teacher, Prof. Dr. Ad. Claus, I have been enabled to add a few new compounds and facts to our present knowledge. To further knowledge concerning their constitution, I have been aided by Prof. Dr. A. Michaelis.

It has been found that substitution in the quinoline ring exerts a great influence on the formation and stability of the ammonium hydroxides. How they are affected by the methyl and phenyl groups when in the α and γ positions has been especially studied in the present work. The close connection existing between the quinoline nitrogen atom and the α and γ carbon atoms has already been shown by the alkyl bases previously made. In my endeavor to prove this relation with greater accuracy the alkyl bases, and their behavior on oxidation, of the following compounds have been particularly investigated:

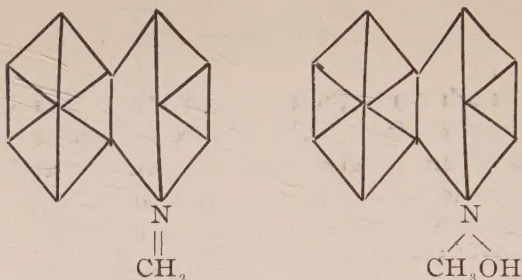
Quinaldine, α -Phenylquinoline, α - γ -Dimethylquinoline, γ -Phenylquinaldine and Flavoline.

In order to complete this study α - γ -Diphenylquinoline is still necessary, but in the present work I was unable to obtain it, although repeated efforts were made to do so.

By the action of sodium hydrate on the ammonium iodides of Quinoline compounds there results easily oxidizable bases. This reaction is entirely different from the result obtained with Diphenyl-dimethyl-ammonium iodide which gives no reaction even on distillation with caustic potash solution. With silver hydrate we also obtain easily oxidizable bases from the Quinoline ammonium iodides, which differ essentially from those produced by sodium hydrate. On treating Diphenyl-dimethyl-ammonium iodide with moist silver oxide we obtain the corresponding ammonium hydroxide. In order to explain this difference Claus¹ has designated one the Methylene base and

¹Jour. Pkt. Chem.

the other the ammonium hydroxide. They having respectively the following structural formulas :



By the action of sodium hydrate hydrogen plus iodine is eliminated, while by means of silver oxide the iodine atom is substituted by hydroxyl as with Tetramethyl-ammonium iodide. The cause of this reaction with sodium hydrate must be the entrance of the nitrogen atom into the benzene ring, imparting a slight electro-negative character to the latter, as in order for nitrogen to be pentavalent at least one of its valencies must be saturated by an electro-negative radicle.

When the γ -hydrogen atom of the quinoline ring is substituted by the carboxyl group we have an easily replacable hydrogen atom present connected with a strong electro-negative group. This has been shown by Claus by numerous examples with Cinchoninic acid iodo-methylate¹ and its substituents² to form a betain. With Carbostyryl we have a similar action. When other positions are occupied by such groups this action does not take place, proving the close connection between the nitrogen and the α and γ carbon atom. Claus mentions³ the possibility of all alkyl bases insoluble in ether (after treatment with potash solution) not being oxidizable to Quinolons and gives one example. This would make the bases oxidized always containing an alkylene group attached to the nitrogen atom.

In the structural formula for a Quinolon assumed by Decker⁴ an oxygen atom is doubly bound to the α or γ carbon atom which on its entrance must break up the inner Quinoline ring linkage. Now it would seem highly improbable that the

¹ Ann. **270**, 335.

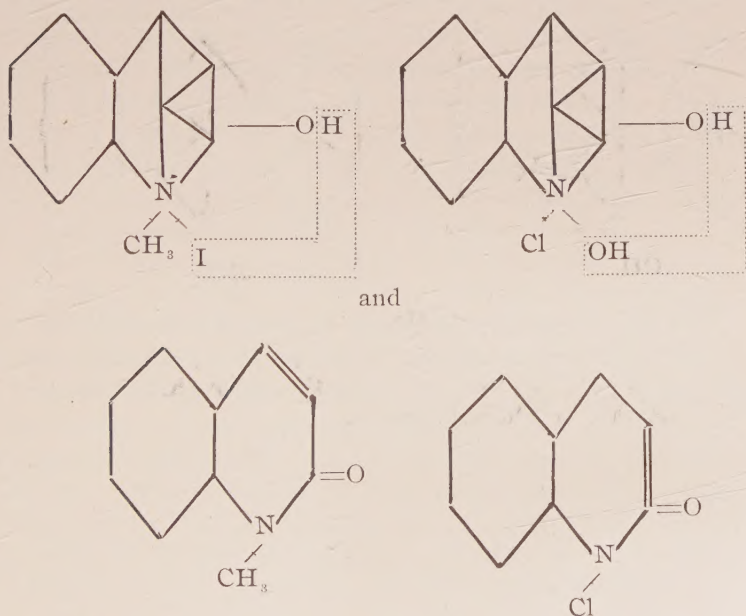
² Ann. **277**, 266-282.

³ Jour. Pkt. Chem. **46**, 119.

⁴ Jour. Pkt. Chem. **45**, 167.

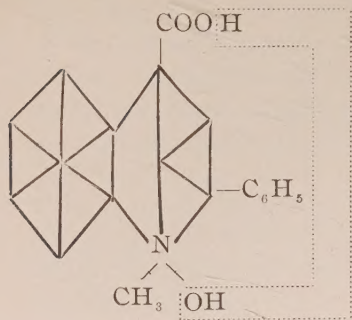
strong electro-negative oxygen atom would be attracted entirely to a position comparatively stable, but would certainly be attached by at least one of its valencies to the nitrogen atom, as is the case with a betain. From what is already known and the further proof contained in this paper the other bond undoubtedly replaces the hydrogen in the α position and when that is occupied by a stable group the hydrogen atom in the γ position, and when both those are replaced by stable groups oxidation cannot take place. This is proven by Decker in his attempts to obtain a Quinolone from Phenylacridine-iodo-methylate¹. In the absence of the evidence which could be furnished by α - γ -Diphenyl quinoline this must be accepted although it should be noticed that the β position is occupied as well as the α and γ . It is therefore possible that this hydrogen might also react, but with greater difficulty if the α and γ positions were both occupied by groups which resisted oxidation.

Granting the intermediate formation of carbostyryl we have according to Decker who made the comparison with ps-chlor-carbostyryl the following :

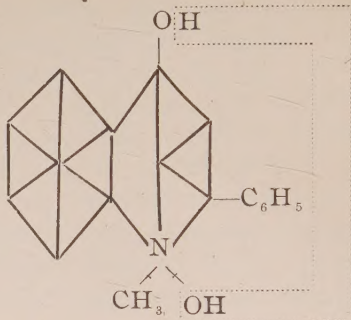


¹ Jour. Pkt. Chem. 45.

Now, instead of making the comparison with ps. chlor-carbostyryl it would seem to me to stand in much nearer relation to the betains. Making the comparison with γ Phenylcinchoninic acid iodo-methylate.

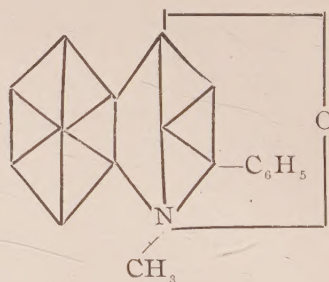
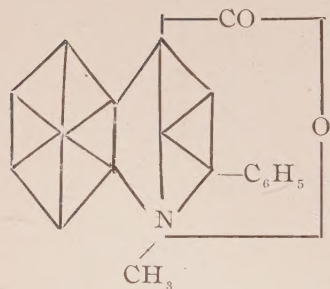


Betain.



Quinolol.

and



This latter formula could also be formed without imagining the intermediate formation of an oxyquinoline, therefore it appears an easier way of clearing up the composition of that class of derivatives called Quinolons.

Preparations Used in the Work.

α-γ-Dimethylquinoline was prepared according to the method of Combes¹ in the following manner: 250 grms. of aluminium chloride were gradually introduced into a large flask fitted with reflux condensor containing 434 grms. of Acetylchloride and 1434 grms. of chloroform. The reaction is very violent owing to the great volume of hydrochloric acid gas liberated. The aluminium chloride at first dissolves but soon a semi-pasty, reddish yellow mass separates out. The chloroform is next boiled until hydrochloric acid ceases to be given off. The separated mass $(\text{CH}_3.\text{CO})_2\text{CH}.\text{CCl}_2.\text{OAlCl}_2$ is freed from the most of the chloroform by distillation. It is best to allow some chloroform to remain.

The reddish yellow crystalline mass was converted into *Acetylacetone* by slowly pouring 8-10 parts of water directly into the residue contained in the flask. This must be done under ice cooling. The reddish aqueous solution was then quickly shaken out with chloroform as acetylacetone decomposes rapidly in acid aqueous solution. The dehydrated chloroform solution was next fractionated and on repeated distillation there was obtained 20-30 grms. which went over between 133-140°. This fraction was used as pure acetylacetone without further purification. Acetylacetone was also made by the method of Claisen² and good results obtained.

¹ Annales die Chemie et de Physique [6] **12**, 207.

² Ber. d. Chem. Ges. xxii, 1011.

Acetylacetone-anilide was next prepared by allowing equivalent quantities of acetylacetone and aniline—after thorough mixing—to stand for several days in a vacuum over sulphuric acid. It solidified to a yellow crystalline mass, which was dissolved in hot, rather dilute alcohol and obtained in pure yellow crystals.

It was endeavored to prepare α - γ -Dimethylquinoline from acetylacetoneanilide by heating to a temperature of 100° for several hours, also by melting with solid caustic potash. Both attempts proved practical for small quantities, but when larger portions were brought into reaction the transformation was very incomplete, therefore the method of Combes was used, viz.: Acetylacetoneanilide was dissolved in 4-5 times its weight of concentrated sulphuric acid and heated on a steam bath until a portion gave no precipitate with water. The mixture was then poured slowly into a large round-bottomed flask containing a solution of sodium hydrate and the free oily base which separated distilled with steam. The distillate was shaken out with ether and after dehydration with solid caustic potash a fraction was obtained distilling between 263 – 269° . A clear, slightly blue fluorescing liquid which was practically pure α - γ -Dimethyl quinoline.

α - γ -Dimethyl-quinoline-iodo-methylate was prepared by allowing α - γ -Dimethyl-quinoline and methyl iodide—necessary excess—to stand in a closed vessel for about one week. The pure light yellow crystalline mass after the excess of methyl iodide had evaporated had a melting point of 226 – 7° . As this was the same as given by Beyer,¹ the mass was used directly without purification.

α - γ -Dimethyl-quinoline-iod-ethylate was prepared according to the method of Beyer,² by heating a mixture of the two constituents in a sealed tube for several hours in a steam bath. The impure crystalline mass obtained was purified by re-crystallization from hot alcohol.

γ -Phenyl-quinaldine was prepared according to the method of Beyer³. It was first necessary to prepare *Benzoylacetone-*

¹ Jour. Pkt. Chem. **33**, 406.

² Ibid.

³ Ber. d. Chem. Ges. XX 1770.

anilide. This was made by both the methods given by Beyer ; I. By heating a mixture of benzoylacetone and aniline to a temperature of 150° until no more aqueous vapor was given off (6-8 hrs. are necessary). II. By boiling with glacial acetic acid for several hours—and a yield of 55-60 % obtained having a melting point of 114° . In addition to the methods given above the condensation was found to take place in the following simple manner: 32.4 grms. Benzoylacetone were mixed to a cream with 18.6 grms. aniline in a large crystallizing dish. The dish was then allowed to stand in a sulphuric acid desiccator for twenty-four hours. At the end of this time the pasty mass had completely crystallized in light yellow plates. These were re-crystallized from hot dilute alcohol and were found to be pure benzoylacetone-anilide. The yield of recrystallized product was 28-30 grms., the same as obtained by the methods of Beyer.

The further condensation of benzoylacetone and aniline to γ -Phenylquinaldine was made as follows: One part of benzoyl-acetone-anilide and 10 parts of sulphuric acid were heated together on a water bath until a portion gave no precipitate when mixed with water ($\frac{3}{4}$ hours were required). The sulphuric acid solution was poured—after cooling—slowly into 20-30 parts of ice water. The brownish, blue fluorescent solution was filtered to free from a slight flocculent precipitate and the γ -phenyl-quinaldine precipitated by the addition of ammonium hydrate to the ice cold solution. The ammonia must be added very slowly as the heat generated by the neutralization otherwise causes decomposition. This is especially the case after the freed base begins to separate and if the dilute ammonia solution be added faster than a drop per minute the white flocculent precipitate melts and forms a partially decomposed sticky mass. If this takes place it is advisable to allow it to stand until the harz solidifies; then proceed with more caution with the addition until no more precipitate is formed. The white flocculent precipitate when dried was found to have the melting point (100°) given by Beyer and was used directly. 12-15 grms. of γ -Phenylquinaldine were obtained from 28-30 grms. of benzoyl-acetone-anilide.

α -Phenyl-quinoline was prepared according to the method

of Döbner and Geisecke¹ from α -Phenyl-cinchoninic acid² by distillation after mixing with 5-6 times its weight of soda lime. The α -phenylquinoline distilled over as a yellowish oil which quickly solidified. The characteristic smelling distillate was dissolved in hot alcohol, and water added to the solution until a small precipitate was formed. On allowing the solution to stand a few hours in a refrigerator there separated a bria of nearly pure white needles which on drying in a small dessicator over caustic potash for several days— α -phenylquinoline volatilizes slowly at the ordinary temperature—were found to have the correct melting point 83° . *α -Phenyl-quinoline-iodo-methylate*³ was prepared by heating α -phenyl-quinoline and methyl iodide (necessary excess) in a closed tube to a temperature of 100° for one-half hour. The dark red crystalline mass was purified by re-crystallization from hot water solution and obtained in orange colored, thick plates having a melting point of 198° .

Through the kindness of Prof. Claus, I obtained flavoline hydrochloride, from which the free base was easily obtained by neutralization of the aqueous solution with ammonium hydrate under good ice cooling.

Flavoline-iodo-methylate was made by the method of Bernthsen & Hess⁴, by heating the two constituents in a closed tube for several hours and crystallizing the product from hot aqueous solution. It crystallizes in yellow plates which melt with decomposition at $192-3^{\circ}$.

¹ Ann. **242**, 294.

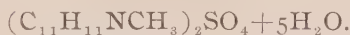
² Through the kindness of Herrn Mükner, who was working with it, I was enabled to make it quickly.

³ Döbner & Miller. Ber. XIX, 1198.

Ber. d. Chem. Ges. XVIII 34.

ALKYL DERIVATIVES OF α - γ -DIMETHYL- QUINOLINE.

α - γ -Dimethyl-quinoline-sulpho-methylate.



Solutions of α - γ -dimethyl-quinoline-iodo-methylate (2 molecules) and silver sulphate (1 molecule) on being mixed produce a voluminous precipitate of silver iodide. This was filtered off and the filtrate evaporated to dryness on a water bath. The whitish residue was dissolved in a little alcohol and after the necessary boiling with animal charcoal crystallized in a bria of white needles on the introduction of ether. The compound proved to be rather unstable, oxidizing slowly at the ordinary temperature with formation of a red color derivative. It has no definite melting point but begins to decompose at 105° . It grows darker and finally melts at a temperature above 210° . The aqueous solution has a blue fluorescence. It is very soluble in alcohol and insoluble in ether.

Analysis.

.1251 grms. sub. gave 0.0551 grms. Ba SO_4 .

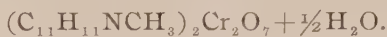
Theoretical: 18.30% SO_4 . Found: 18.14% SO_4 .

Water determination.

On heating 0.2358 grms. of substance for two hours to a temperature of 105° , it lost 0.0420 grms.

Theoretical: 16.98% H_2O . Found: 17.77 H_2O .

As the compound was a good deal decomposed the result is not considered exact.

α - γ -Dimethyl-quinoline-chromo-methylate.

On pouring a warm concentrated solution of the corresponding iodide (2 molecules) into a solution of bichromate of potash (1 molecule) a heavy precipitate of orange yellow needles is formed, more and more separating as the solution grows cold. It is slightly soluble in cold water and decomposition results on boiling the aqueous solution. Soluble in alcohol. Reduction takes place on heating the solution, chromic oxide being precipitated. It is insoluble in Benzol. Violent decomposition takes place on heating to 175° . Carbon and chromic oxide remaining.

Analysis.

The chromium determination was made by gently heating in a large closed crucible. Pure chromic oxide being finally obtained after glowing. 0.2566 grms. sub. gave 0.0691 grms. Cr_2O_3 .

Theoretical: 18.39% Cr. Found: 18.46% Cr.

Water determination.

0.2566 grms. substance lost 0.0052 grms. on being heated 4 hours to a temperature of 110° .

Theoretical: 1.68% H_2O . Found: 2.03% H_2O .

 α - γ -Dimethyl-quinoline-chloro-methylate.

To an aqueous solution of α - γ -Dimethyl-quinoline-iodo-methylate there was added an excess of the calculated amount of moist, freshly precipitated silver chloride. The flask and contents were heated to the temperature of the water bath and shaken constantly for three-quarters of an hour. The white silver chloride became gradually yellow, showing the formation of silver iodide. After filtration the filtrate was evaporated to dryness and the residue dissolved in a little alcohol. Long, yellowish needles were obtained on the introduction of ether. α - γ -Dimethyl-quinoline-chloro-methylate is too soluble in water and alcohol to crystallize from these solutions, but is insoluble in ether.

Analysis.

0.0931 grms. substance gave 0.0535 grms. Ag Cl.

Theoretical: 14.40% Cl. Found: 14.21% Cl.

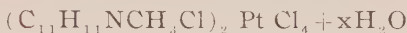
The compound being a simple salt, all the chlorine was precipitated by introduction of silver nitrate excess to the acidified solution.

Water determination.

0.0733 grms. substance lost 0.0108 grms. in weight on being heated to a temperature of 110° for 3 hours.

Theoretical: 14.59%. Found: 14.81% H₂O.

The melting point was 268°.

The Platinum double salt.

was precipitated after allowing a dilute hydrochloric acid solution of α - γ -Dimethyl-quinoline-chloro-methylate and platinum chloride to stand for some time. The straw yellow, microscopic, tetragonal plates which were formed had a melting point of 257°.

ACTION OF NaOH ON

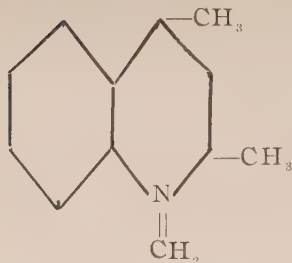
 α - γ -DIMETHYL-QUINOLINE-iodo-METHYLATE.

On treating a cold aqueous solution of α - γ -Dimethyl-quinoline-iodo-methylate with a few drops of a dilute sodium hydrate solution it is colored a yellowish brown. If the solutions be concentrated there separates a yellowish oil. By allowing the yellowish brown solution to stand, or immediately on warming a deep blue harz separates. The yellowish oil forms a similar harz by the same treatment, the oily drops on the surface being almost immediately oxidized by air contact. In order to prevent this a solution of the iodo-methylate was placed in separatory funnel and covered with a layer of ether. A small quantity of sodium hydrate was added and the mixture shaken. The ether took on a brown color leaving a perfectly clear aqueous layer beneath which was found to contain only sodium hydrate excess.

The brownish yellow ethereal solution was washed by shaking with a little pure water and a portion allowed to evap-

orate spontaneously. There remained a yellowish oil which according to the theory of Claus is

α - γ -Dimethyl-quinoline-methylene-base.



It was almost immediately oxidized first to a brown, then green and finally a dark blue solid mass. This residue was soluble in alcohol to a deep purple blue solution.

The bluish harz obtained by allowing the impure aqueous solution to stand is also soluble in alcohol forming a deep purple blue solution.

This was noticed by Beyer¹ and supposed by him to be a "Cyanin;" but owing to the fact of its being formed after all traces of iodine were removed as well as before it was undoubtedly this simple oxidation product.

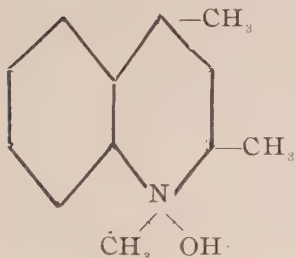
It was endeavored to obtain crystals of the blue dye base, or to oxidize it further to a quinolon (as is possible with some corresponding quinoline derivatives) by evaporation to dryness of the alcoholic solution. This was repeated *ten times* nothing however but a blue black residue was obtained. It dissolved in hydrochloric acid to a nearly-clear solution forming the chloride of the dye base whose composition does not concern the present work. The fact that this color derivative was not further oxidized by air contact would seem to indicate that no quinolon resulted when the α and γ positions were both occupied but this will be discussed more fully at another place.

The remainder of the ethereal solution was shaken out with a little hydrochloric acid. It was immediately discolored. The hydrochloric acid solution was drawn off, evaporated to dryness on a water bath and the white residue dissolved in alcohol. From the latter solution thick, yellowish needles were obtained by the introduction of ether, which were found to have a melting point of 268° showing them to be identical with the chloride obtained by the action of silver chloride on the iodide. In order to further prove this identity the platinum double salt was made. Its melting point was 257° .

¹ Jour. Pkt. Chem. **33** 406.

ACTION OF Ag_2O on α - γ -DIMETHYL-QUINOLINE-iodo-METHYLATE.

An excess of the calculated quantity of freshly precipitated moist silver oxide was placed in a mortar containing a solution of α - γ -Dimethyl-quinoline-iodo-methylate with some of the latter in excess not dissolved. After quick but thorough agitation a portion of the solution gave no precipitate with silver nitrate showing that all the iodine had been converted into insoluble silver iodide. It was then filtered and a perfectly clear—slightly blue from oxidation—strongly alkaline solution of

 α - γ -Dimethyl-quinolinium-methyl hydroxide

obtained.

On shaking this alkaline aqueous solution with ether the ether took on a yellow color, but proved on evaporation to contain but a very small quantity of yellowish oil which was almost immediately oxidized to a green, and after some time, blue color base. The concentra-

ted alkaline solution was shaken out repeatedly with ether, and each time on evaporation—after washing the ethereal solution carefully with water—the ether was found to contain some of the base, although the quantity diminished.

In order to see if there was any difference between this ethereal solution and that obtained by the action of sodium hydrate one of the extracts was divided into two portions. One portion was shaken with a solution of sodium hydrate and allowed to evaporate spontaneously while the other was evaporated without this addition. No difference was to be noticed between them or in the residues left on evaporation.

The alkaline ethereal solution was also shaken out with pure, cold water, but no alkaline reaction was imparted to the latter, showing that the ammonium hydroxide had lost its solubility in water.

The strongly alkaline, aqueous solution of the ammonium hydroxide yielded an oily precipitate, on the addition of concentrated caustic potash solution, of the methylene base.

A portion of the aqueous alkaline solution was neutralized with hydrochloric acid. The chloride thus obtained was purified as previously described. A portion of the yellow ethereal solution was also shaken out with hydrochloric acid and the chloride obtained from this source. Their melting points proved them to be the same as those obtained by the action of silver chloride on the iodo-methylate.

ACTION OF SODIUM ETHYLATE ON THE BASE.

In this experiment it was endeavored to make the ethyl ether. α - γ -Dimethyl-quinoline-iodo-methylate was dissolved in absolute alcohol in which a slight excess of the calculated quantity of metallic sodium had been dissolved. The solution was allowed to stand in a corked flask for some time. The colorless solution became a brown, then a blue color which continued to deepen on long standing. A portion of the solution was evaporated on a water bath, but only a dark blue harz was obtained. The remainder was evaporated cold in a vacuum over sulphuric acid with a similar result, showing that no ester was formed.

α - γ -Dimethyl-quinoline-chrom-ethylate.



Warm solutions of α - γ -Dimethyl-quinoline-iodo-methylate and potassium bichromate—proper proportions being observed—were brought together. The slight separation of harz was removed by filtration. A bria of star-shaped, orange yellow needles separated on cooling. These were filtered off, washed with cold water and dried for analysis.

Water determination.

0.1796 grms. substance was heated to 110° for eight hours before constant weight was obtained, losing 0.0269 grms.

Theoretical: 1.44% H_2O . Found: 1.49% H_2O .

This chromate is very soluble in hot water, somewhat in cold, to a yellow solution. It is also soluble in alcohol, but no reduction takes place on warming the solution as is the case with the methylchromate. It has no definite melting point but gradually decomposes at a temperature above 230° . Several

chromium determinations were made but from 1-2 % too much was always found.

If an excess of potassium bichromate is used there separates out on the cooling of the solution, bright red crystals of the *Acid chromate* $C_9H_5(CH_3)_2NC_2H_5 \cdot HCr_2O_7 + xH_2O$, which is much more soluble in cold water than the normal chromate and decomposes violently at a temperature of less than 150° .

On treating α - γ -Dimethyl-quinoline-iodo-methylate with moist silver chloride in the same manner as with the corresponding methyl derivative there results

α - γ -Dimethyl-quinoline-chlor-ethylate.



It was obtained in thick, white, stellar needles by the introduction of ether into the alcoholic solution which melted in their water of crystallization at a temperature of $70-80^\circ$. The dehydrated salt melts at 212° .

Analysis.

0.2487 grms. substance gave 0.1337 grms. Ag Cl.

Theoretical: 12.85% Cl. Found: 13.29% Cl.

Water determination.

I. 0.0943 grms. substance lost 0.0184 grms.

II. 0.2489 grms. substance lost 0.0475 grms.

When heated to a temperature of $110-115^\circ$ for six hours—constant weight being obtained.

Theoretical: 19.61% H_2O . Found: I. 19.51% H_2O .
II. 19.09% H_2O .

On addition of platinic chloride to the hydrochloric acid solution there separated a fine yellowish or flesh-colored precipitate of the *Platinum double salt* $(C_{11}H_{11}NC_2HCl)_2PtCl_4 + xH_2O$ which on removal by filtration was found to consist of a mass of microscopic, orthorhombic plates, having a melting point of $232-233^\circ$.

α - γ -Dimethyl-quinoline-sulpho-ethylate.



When hot solutions of α - γ -Dimethyl-quinoline-iod-ethylate (2 molecules) and silver sulphate (1 molecule) are

brought together there is produced a heavy precipitate of yellow silver iodide. This was filtered off and the blue fluorescent solution evaporated to dryness on a water bath. The residue was dissolved in alcohol and after the necessary treatment with animal charcoal crystallized out by the introduction of ether. The white crystalline needles obtained were found to be very soluble in cold water and alcohol, but insoluble in ether the same as nearly all this series of salts. It melts with decomposition at 208° .

Analysis.

0.1809 grms. substance gave 0.0924 grms. BaSO_4 .

Theoretical: 20.51% SO_4 . Found: 21.03% SO_4 .

Water determination.

0.1558 grms. substance lost in CaCl_2 dessicator in twenty-four hours 0.0096 grms. In sixty-two hours 0.0154 grms. The same on being heated for two hours to 110° lost 0.0003 grms. additional.

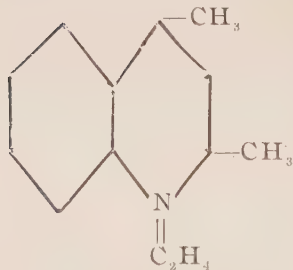
Theoretical: 10.34% H_2O . Found: 10.07% H_2O .

ACTION OF NaOH on

α - γ -DIMETHYL-QUINOLINE-IOD-ETHYLATE.

On adding a few drops of sodium hydrate to a cold solution of α - γ -Dimethyl-quinoline-iod-ethylate there immediately separates a light yellow oily precipitate which in all probability is

α - γ -Dimethyl-quinoline-ethylene base.



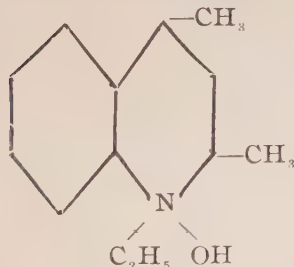
It is somewhat more stable than the corresponding methylene base but begins to oxidize shortly on exposure to the air with formation of a blue harz. This harz was found to be soluble in alcohol to a deep purple blue solution.

In order to prevent all decomposition a solution of the iod-ethylate was placed in a separatory funnel and after the introduction of a layer of ether a little sodium hydrate added. On shak-

ing, the ethereal layer took on a yellow color leaving the watery layer perfectly clear. The yellow ethereal solution was shaken out with hydrochloric acid—immediately decolorized. The hydrochloric acid solution was evaporated to dryness and the chloride crystallized in the usual manner. The melting point obtained was $208-9^{\circ}$ while the same salt produced by the action of silver chloride had a melting point of 212° . This difference was probably due to impurity. In order to further prove the identity of these two chlorides the platinum double salt was made. It was found to have a melting point of 234° .

ACTION OF MOIST Ag_2O ON α - γ -DIMETHYL-QUINOLINE-IOD-ETHYLATE.

Freshly prepared moist silver oxide and α - γ -Dimethyl-quinoline-iod-ethylate were rubbed together in a mortar containing an aqueous solution of the latter until a portion on filtration failed to react with silver nitrate. The whole was then quickly filtered into a separatory funnel containing some absolute ether. The clear—slightly blue from oxidation—strongly alkaline filtrate of *α - γ -Dimethyl-quinolinium-ethyl-*



hydroxide, was then shaken thoroughly with the ether. The latter immediately assumed a pale yellow color showing that some part of the should be insoluble ammonium oxyhydrate had been dissolved. The watery layer was drawn off and was found to still react strongly alkaline. The ethereal solution also turned red

litmus paper blue and a portion on spontaneous evaporation left a goodly quantity of yellowish oil which oxidized to a dye base on standing. The alkaline aqueous solution was shaken out again with ether and again a yellow ethereal solution was obtained. This was repeated six times. The series of extracts were placed in crystallizing dishes in rotation and each—taking them in order—left less residue than the preceding. The aqueous solution remaining still reacted alkaline, so was neutralized with hydrochloric acid and evaporated to dryness. A

very small white residue of the chloride remained but the major part of the ammonium hydroxide had been dissolved by the repeated extractions with ether.

A strong ethereal solution of the same was shaken with pure water. No alkaline reaction was imparted to the latter. Another portion was shaken with a dilute solution of sodium hydrate and allowed to evaporate. No difference was to be observed between this residue and that of those which had not been so treated.

A portion was converted into the chloride and platinum double salt. These as was to be expected had the same melting points as those made by the action of silver chloride on the iodide of the base, viz. : 212° and 233° .

α - γ -Dimethyl-quinolinium-ethyl-hydroxide is very soluble in water ; and is either very readily dehydrated by or soluble in absolute ether. It is much more readily soluble in the latter reagent than the corresponding methyl hydroxide and is not so quickly oxidized by air contact.

ALKYL DERIVATIVES OF γ -PHENYL-QUINALDINE

γ -Phenyl-quinaldine-iodo-methylate,



Was prepared by heating γ -Phenyl quinaldine with the necessary excess of methyl iodide in a sealed tube for several hours at a temperature of 100° . The red—from formation of polyiodides—crystalline mass was purified by recrystallization from hot water solution. Slim yellow needles separated on cooling which were found to contain $\frac{1}{2}$ molecule of crystal water.

Water determination.

0.1362 grms. substance lost 0.0031 grms. in weight on being heated for three hours to a temperature of 110° .

Theoretical : 2.43% H_2O . Found : 2.27% H_2O .

It crystallizes from absolute alcoholic solution in flat, yellow, anhydrous needles. No loss of weight resulted on heating for several hours at 110° . An iodine determination of the same gave :

Analysis :

0.3590 grms. substance gave 0.2294 grms. AgI.

Theoretical : 35, 23% I Found : 34.82% I.

γ -Phenyl-quinaldine-iodo-methylate is very soluble in hot water, rather soluble in cold, very soluble in alcohol and insoluble in ether. It melts without decomposition at 203°.

Combustion :

I. 0.1834 grms. substance gave 0.0767 grms. H_2O .

Theoretical : 4.59% H. Found : 4.64% H.

II. 0.1563 grms. substance gave 0.0656 grms. H_2O and 0.2931 grms. CO_2 .

Theoretical . 4.59% H. Found : 4.61% H.

“ 50.57% C. “ 51.11% C.

III. 0.2259 grms. substance gave 0.0925 grms. H_2O and 0.4214 grms. CO_2 .

Theoretical : 4.59% H. Found : 4.51% H.

“ 50.57% C. “ 50.42% C.

 γ -Phenyl-quinaldine-iod-ethylate.

Was prepared by heating γ -Phenyl-quinaldine with an excess of ethyl iodide to a temperature of 100° for several hours in a closed tube. The product was very impure. It was first crystallized from hot alcoholic solution, and further by dissolving again in alcohol and crystallization by the addition of ether.

It is soluble in cold water, very soluble in hot. Soluble in alcohol, crystallizing from the solution in anhydrous needles and is insoluble in ether.

Analysis.

0.3022 grms. substance gave 0.1841 grms. AgI.

Theoretical : 33.68% I. Found : 33.23% I.

It melts with decomposition at 185-186° C.

 γ -Phenyl-quinaldine-sulpho-methylate.

This salt was made by mixing a hot concentrated solution of silver sulphate (1 molecule) with a solution of γ -Phenyl-

quinaldine-iodo-methylate (2 molecules). The silver iodide which separated was filtered off and the solution containing γ -Phenyl-quinaldine-sulpho-methylate was evaporated to small bulk on a water bath—If evaporated to complete dryness decomposition results—and allowed to crystallize. It separated out in long white needles which on removal from the solution immediately oxidized, becoming a blue green color. They were dissolved in absolute alcohol to free from any silver sulphate excess and recrystallized by the introduction of ether. It was endeavored to decolorize a portion of the green alcoholic solution by boiling with animal charcoal, but further oxidation resulted. From the colored alcoholic solution colorless needles were again obtained by covering with a layer of ether and allowing to stand for several days in a closed vessel. These were removed by filtration, washed with ether and dried on a porous plate as quickly as possible. A sulphur determination of the greenish blue mass gave the following result, calculating for 5 H_2O .

Analysis :

0.1298 grms. substance gave 0.0446 grms. BaSO_4 .

Theoretical: 14.67% SO_4 . Found: 14.15% SO_4 .

It was attempted to make a water determination but no satisfactory result could be obtained owing to decomposition. γ -Phenyl-quinaldine-sulpho-methylate is very soluble in cold water and alcohol; is insoluble in ether and melts in its water of crystallization at $80-90^\circ$ with decomposition. It solidifies on drying to a black mass which melts again at a temperature above 200° .

On bringing together warm solutions of γ -phenyl-quinaldine-iodo-methylate (2 molecules) and potassium bichromate (1 molecule) there separates small, orange yellow needles of

γ -Phenyl-quinaldine-chromo-methylate.



It decomposes with explosion when heated to a temperature above 150° , leaving carbon and chromic oxide as residue. It is slightly soluble in cold water, more so in hot. It is soluble in alcohol.

Analysis.

0.0981 grms. Substance gave 0.0211 grms. Cr_2O_3 on ignition.

Theoretical: 14.91% Cr. Found: 14.75% Cr.

Water determination.

0.0981 grms. Substance lost, 0.001 grms. when heated for five hours to a temperature of 100° .

Theoretical: 1.29% H_2O . Found: 1.02% H_2O .

 γ -Phenyl-quinaldine-chloro-methylate.

Freshly precipitated, finely divided silver chloride in necessary excess was added to a hot aqueous solution of the corresponding iodide contained in a small flask. It was thoroughly shaken for one hour while the contents were kept at a temperature of nearly 100° . After allowing it to stand over night the silver iodide formed and silver chloride excess were filtered off, the filtrate evaporated to dryness on a water bath and the residue dissolved in alcohol. From the solution, on the addition of ether, well formed, flat, yellowish crystal needles were obtained.

Analysis.

0.1842 grms. substance gave 0.0812 grms. Ag Cl.

Theoretical: 10.94% Cl. Found: 10.90% Cl.

Water determination.

0.1916 grms. substance lost 0.314 grms when heated to a temperature of $105-115^\circ$ for six hours constant weight was obtained.

Theoretical: 16.69% H_2O . Found: 16.38% H_2O .

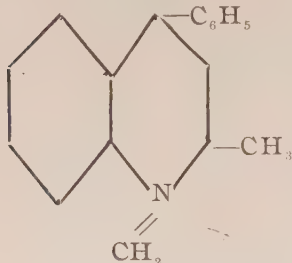
It is very soluble in cold water and alcohol but insoluble in ether. It melts in its water of crystallization at a temperature of 90° . The dehydrated salt melts with decomposition at 245° .

On the addition of platinic chloride to the hydrochloric acid solution there immediately separated a yellowish white precipitate of the *Platinum double salt* $(\text{C}_9\text{H}_5\cdot\text{C}_6\text{H}_5\cdot\text{CH}_3\text{NCH}_3\text{Cl})_2\text{Pt Cl}_4$ which on examination under the microscope showed no crystallization. It melts with decomposition at a temperature of 250° .

ACTION OF NaOH ON

 γ -PHENYL-QUINALDINE-iodo-METHYLATE.

On adding a few drops of sodium hydrate to a cold saturated solution of γ -Phenyl-quinaldine-iodo-methylate there immediately separates a yellow, oily precipitate of γ -Phenyl-quinaldine methylene base.



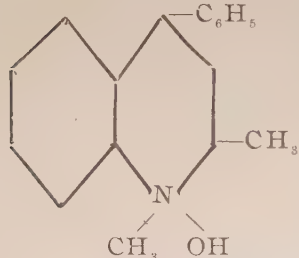
It gradually collected in oily drops which slowly decomposed into a red dye base.

A solution of the iodo-methylate was placed in a separatory funnel, covered with a layer of ether and a little sodium hydrate added. On shaking, the base was readily dissolved by ether to a brownish yellow solution. A portion of the ethereal solution was evaporated spontaneously and a brownish black, oily residue obtained. Another portion was evaporated in a vacuum over sulphuric acid. A yellowish, oily residue which gradually oxidized to a brownish red harz remained. This harz was found to dissolve in alcohol to a clear, slightly red solution. By repeatedly dissolving in alcohol and evaporating the color deepened to a red black on account of further oxidation but no crystals of the dye base were obtained and oxidation to a quinolon did not result. The remainder of the ethereal solution was treated with dilute hydrochloric acid. It was immediately decolorized. The hydrochloric acid layer was evaporated to dryness on a water bath, the residue dissolved in alcohol and by addition of ether the weakly yellow, crystal needles of the chloride obtained. These after dehydration were found to have a melting point of 247° —decomposition. The platinum double salt was also made and was found to melt with decomposition at a temperature of 250° .

ACTION OF MOIST Ag_2O on γ -PHENYL-QUINALDINE-iodo-METHYLATE.

Freshly precipitated silver oxide and γ -phenyl-quinaldine-iodo-methylate were placed in a mortar together with a little

water and rubbed for a very short time. A portion of the solution on filtration gave no reaction with silver nitrate and reacted strongly alkaline with Tumeric paper. The entire solution was then quickly filtered into a separatory funnel and a clear--colored slightly by oxidation—solution of *γ-Phenyl-methyl-quinaldinum-hydroxide* obtained. This solution on shaking



out with ether imparted to the latter a yellow color and a portion on evaporation left a very slight oily residue which on standing exposed to the air soon oxidized to a red dye base. The portion dissolved by the ether was probably not more than from one to five per cent. of the ammonium hydroxide contained in the solution.

The alkaline ethereal solution on shaking with pure cold water imparted no alkaline reaction to it, and on shaking with a solution of sodium hydrate and allowed to evaporate no difference is to be noticed in the residue. This fact taken together with that that no alkaline reaction was imparted to water on shaking—owing to the great dilution of the ethereal solution this may not have had any value—it would seem to indicate that a small quantity of the ammonium hydroxide had been dehydrated by the ether and converted into methylene base.

By neutralization with hydrochloric acid, evaporation to dryness and recrystallization from alcohol by the introduction of ether, (after the necessary handling with animal charcoal) clear yellow needles of the chloride were obtained. These after dehydration melted at a temperature of 244° .

ALKYL DERIVATIVES OF FLAVOLINE.

Flavoline-sulpho-methylate.



Was prepared in the ordinary manner from the iodide and silver sulphate. After the removal of the silver iodide there remained a bright yellow solution of Flavoline-sulpho-methylate. This was evaporated to dryness—decomposes if evapora-

ted to complete dryness—and placed in a sulphuric acid desiccator. After standing 3-4 days a thick yellow syrup remained which on long standing did not crystallize. It was dissolved in absolute alcohol and the solution covered with a layer of ether (water free). There slowly separated an oily precipitate. The process was repeated but no crystals were obtained.

When cold solutions of bichromate of potash and flavoline-iodo-methylate are brought together there separates a yellow flocculent precipitate of

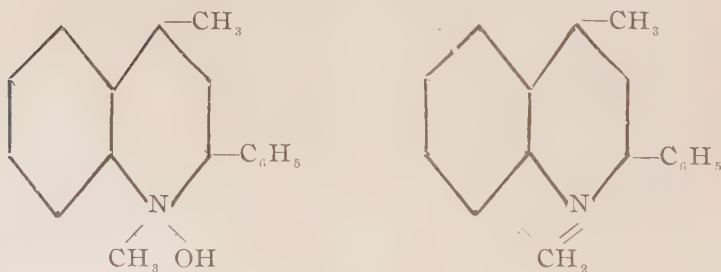
Flavoline-chromo-methylate.



If hot solutions be used there separates a reddish yellow precipitate which on standing several hours crystallizes in reddish yellow plates which decompose slowly when heated above 100° .

ACTION OF Na OH AND Ag_2O on
FLAVOLINE-iodo-METHYLATE.

Methyl-flavolinium-hydroxide and Methylene base.



By the action of sodium hydrate on flavoline-iodo-methylate there is produced a pure, yellow, oily precipitate. If the iodo-methylate contains traces of polyiodides there results a "braun rother beim Reiben zusammen backender Niederschlag," as stated by Bernthsen and Hess,¹ which dissolves readily in ether showing it to be the methylene base.

On bringing the iodide together with water and an excess of freshly precipitated silver oxide, then rubbed with a pestle

¹ Ber. d. Chem. Ges. XVIII. 34.

for a short time, there is obtained a strongly alkaline solution which does not react with silver nitrate. The clear—slightly colored from oxidation—solution was quickly introduced into a separatory funnel and shaken out with ether. No alkaline reaction was imparted to the ether and on evaporation no residue remained, showing that the ammonium hydroxide had been formed and was *absolutely insoluble in ether*. On treating the aqueous solution with a few drops of sodium hydrate it dissolved readily in the ether to a brownish-yellow solution showing the change to methylene base.

ALKYL DERIVATIVES OF α -PHENYL-QUINOLINE.

α -Phenyl-quinoline-sulpho-methylate.



Was prepared by bringing the two constituents together as mentioned with similar salts. The dry residue left on the evaporation of the blue fluorescent aqueous solution, was dissolved in alcohol and after the necessary boiling with animal charcoal was obtained from the solution on introduction of ether in white crystalline needles. It is very hygroscopic, melting quickly in the moisture it attracts on short exposure to the air.

α -Phenyl-quinoline-chromo-methylate.



fell out as an orange yellow, crystalline precipitate when a warm solution of potassium bichromate (1 molecule) was poured into a warm concentrated solution of α -Phenyl-quinoline-iodo-methylate (2 molecule). It decomposes with explosive violence at a temperature above 205° .

The ammonium hydroxide and methylene base were also made and their properties noted. I am enabled to confirm the work of Büttner¹ the ammonium hydroxide being entirely insoluble in ether until treated with sodium hydrate solution.

¹ Inaugural Dissertation. Freiburg i-B.

BEHAVIOR OF DIFFERENT ALKYL-BASES ON OXIDATION.

As a forerunner to the following work the oxidation of chinolinium-methyl-hydroxide was made as follows: 5 grms. of Quinoline-iodo-methylate were dissolved in 40 C. C. of water and added drop by drop to a cold solution consisting of 15 grms. potassium ferricyanide (in 100 C. C. water) and 40 C. C. of a 10% solution of caustic potash, methyl quinolon¹ was obtained and was found to have a melting point of 71°.

In the following oxidations the same relative concentration of solution was used as given above.

Oxidation of Quinaldine-methylene base².

As the oxidation was rather incomplete at the ordinary temperature it was made at a heat of 30-40°. Momentarily the oily base separated. It was however immediately oxidized to a greenish black insoluble slime which soon became partially crystalline. After the proscribed quantity of quinaldine-iodo-methylate had been added the solution was shaken out with ether. The greenish black color derivative did not dissolve. The yellow ethereal solution was dried with a few pieces of solid caustic potash and the ether allowed to evaporate spontaneously. The residue left was simply unoxidized alkyl base. The black partly crystalline harz was washed with water and dissolved in alcohol. It formed when dilute a beautiful red solution. On spontaneous evaporation of the alcohol there remained a black, purple red residue, which on examination through the sides and bottom of the crystallizing dish had the characteristic green shimmer of a true dye base. In order to see if further oxidation was possible it was dissolved in alcohol and evaporated ten times. No change took place.

Oxidation of α -Phenyl-quinolinium-methyl-hydroxide.

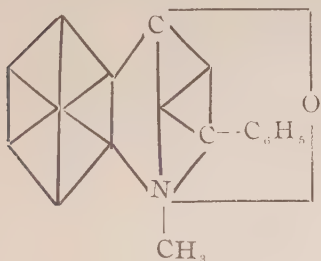
On account of the difficult solubility of the iodide the chloride was used.

No oxidation resulted at the ordinary temperature. When

¹ Decker, Jour. Pkt. 47, 31.

² Quinaldine-iodo-methylate was prepared by heating the constituents together in a sealed tube according to the method of Döhner and Miller. Ber. XVI, 2468.

carried out at a temperature of 30–40° the colorless oily precipitate, which fell out on the introduction of each drop of the chloro-methylate solution, was almost immediately converted into a reddish white flocculent one. As the reaction drew near a close the oxidation was not as rapid and the scarcely momentary formation of a red intermediate color derivative was to be observed. After the α -phenyl-quinoline-chloro-methylate had all been added the solution was thick with the reddish white crystalline precipitate of *α -Phenyl-quinoline-methyl-quinolon* which was found to have a melting point of 107–9°.



It is very soluble in alcohol and benzene, crystallizing but poorly from those solutions in small white needles.

This oxidation also takes place by the standing of the precipitated methylene base in strong alkaline solution for several days.

It dissolves in concentrated hydrochloric acid forming a chloride which on recrystallization from alcohol (by the addition of ether) was obtained in slim white needles which had a melting point of 223–224°. On the addition of platinic chloride to the concentrated hydrochloric acid solution there separated as a fine, flesh colored precipitate the platinum double salt which decomposes at a temperature of 173–177°.

The analysis gave the following result :

Combustion.

0.1475 grms. substance gave 0.0743 grms. of H_2O and 0.4704 grms. of CO_2 .

Theoretical: 5.53% H. Found: 5.59% H.

“ 81.70% C. “ 81.43% C.

Oxidation of α - γ -Dimethyl-quinolinium methyl-hydroxide.

Oxidation to a greenish black harz resulted at the ordinary temperature. The same result was obtained when the temperature was increased. As it had been fully tried to oxidize this dye base further by repeated evaporation of the alcoholic solution (see page 14) it was not attempted here.

A considerable quantity of unoxidized material was obtained on shaking the products of the oxidation with ether.

Oxidation of γ -Phenyl-quinaldinium-methyl-hydroxide.

A heavy brown precipitate is formed if the solutions be brought together quickly, the solution becoming greenish. It was attempted to remove it by filtration. Nothing remained on the filter but a black slime, the quinolon if such it might be being very unstable. The reaction was repeated. Complete decomposition took place on standing a short time in solution. Owing to the extreme instability of this precipitate it was impossible to do anything with it. γ -Phenyl-quinaldinium-methyl-hydroxide having both the α and γ positions occupied would make the formation of its quinolon of unusual interest. On making the addition in the same manner—slowly, drop by drop—as used in the other oxidations of this series the dye base resulted directly.

Oxidation of Methyl-flavolinium-hydroxide.

It was thought that by using flavolinium-methyl-hydroxide a more stable product could be obtained as the phenyl group occupies the α position and would resist secondary oxidation.

No oxidation resulted at the ordinary temperature. On gradual increase of temperature a black harz was formed at 50–60°. Which was not dissolved on shaking the solution with ether—a slight quantity of unoxidized base was obtained from the ether however on evaporation.

The dye base formed a bright green solution with alcohol. By repeated evaporation with alcohol but little further oxidation from air contact resulted. The dye base deepened in color to some extent.

It was endeavored to prepare α - γ -Diphenyl-quinoline it being the intention to make its iodo-methylate, ammonium hydroxide, etc., and finally to see if the ammonium hydroxide was oxidized to a quinolon on treatment with ferricyanide of potassium and caustic potash solution.

According to the results obtained by Decker in his work with phenyl-acridine-methyl-hydroxide¹ no oxidation (Quinolon would result.

¹ Jour. Pkt. Chem. 45, 197.

The only method given for the preparation of α - γ -Diphenyl-quinoline is that of Beyer¹, to be made by the same methods as given for γ Phenyl-quinoline. As γ -phenyl-quinoline had been prepared by both the methods given by Beyer, as well as by a partially new one, with excellent results they were well understood. The method of procedure consists of two parts: First, The partial condensation to anilide. Second, Complete condensation to α - γ -Diphenyl-quinoline.

The condensation to anilide according to Beyer was incomplete. Both methods—boiling several hours with glacial acetic acid and the simple heating of the two constituents (Dibenzoyl methane² and aniline) to a temperature of 150° until no further aqueous vapors are given off—given for it were tried repeatedly. The further condensation to α - γ -Diphenyl-quinoline—made by heating the anilide to 100° with ten parts sulphuric acid for several hours—was attempted both with the raw product direct and after crystallization from alcohol but no α - γ -Diphenyl-quinoline was obtained.

The results more fully given are as follows :

The raw product, obtained after boiling the calculated quantities of Dibenzoylmethane and aniline with ten parts glacial acetic acid for six hours, was dissolved in hot alcohol. Flat, yellow crystals separated from the solution on cooling which had every appearance of an anilide, although the melting point 70–73° showed it to be impure dibenzoylmethane. Several nitrogen determinations were made and it was found to contain from 0.75% to 1.5% while 4.94% nitrogen are theoretically required for the anilide. This proved it to be dibenzoyl-methane, aniline (held mechanically from lowered melting point) and probably some anilide. It was heated with concentrated sulphuric acid (ten parts) for several hours. the mixture poured slowly into ice water. the precipitated harz which separated filtered off and the slightly blue fluorescing liquid shaken out with ether. The ether on evaporation left a white crystalline residue which had a melting point of 121° and on closer examination proved to be benzoic acid. The blue fluorescent liquid was neutralized with ammonia, under ice cooling, and again shaken out with ether. This dehydrated ethereal extract on evaporation left a very slight oily residue, which on solution in hydrochloric acid formed an insoluble chromate and so was doubtless a trace of some quinoline derivative and had caused the blue fluorescence.

Much the same result was obtained with the raw product formed by heating a mixture of dibenzoyl-methane and aniline to a temperature of 150°. The chief difference was that the dibenzoyl-methane was not so much decomposed and that more benzoic acid was formed. A very clear, blue fluorescing solu-

¹ Ber. d. Chem. Ges. XX., 1772

² I take pleasure in thanking Prof. Dr. Claisen at this point for his kindness in sending me some of this preparation. I also made it by his method. Ber. XX. 655.

tion was obtained after filtering off the unchanged dibenzoyl-methane, nothing, however, but a little benzoic acid and an oily residue was obtained from it. On washing the dibenzoyl-methane filtered off with much water it was in part dissolved, forming a blue fluorescing solution. It contained practically nothing however but benzoic acid as shown by the melting point 121° . The melting point given by Beyer for *o-r*-diphenyl-quinoline is 112° .

The difficulty was undoubtedly caused by the failure of the dibenzoyl-methane and aniline to condense to anilide. But very slightly differing results from those given above were obtained on repeated trials. Absolutely no condensation took place in the cold on standing in a sulphuric acid dessicator. Under these conditions the condensation of benzoylacetone and anilide was complete. It was thought that an increase of temperature might effect the condensation, so a mixture of dibenzoyl-methane and aniline (an excess of the required quantity) contained in a small flask with an air reflux condensor, was heated on an oil bath until the aniline was brought to boiling. A little moisture ascended the condensor almost immediately but by continued boiling no more was found. The semi-fluid mixture was treated with cold dilute hydrochloric acid in order to remove unchanged aniline. A melting point determination of the crystalline residue was made and showed it to be impure dibenzoyl-methane. The water which separated was doubtless hygroscopic and not produced by any reaction. A mixture of the two constituents were next heated in a sealed tube to a temperature of $200-210^{\circ}$ for several hours. The unattacked aniline was removed by means of hydrochloric acid as before. A melting point determination of the crystalline residue gave 90° , but on heating with sulphuric acid, etc., nothing was obtained but a black sticky mass, showing that some unknown decomposition had taken place.

As the condensation to an anilide, or at most to a very small extent, did not result, it was concluded that it might result directly by heating with sulphuric acid as is the case with many quinoline compounds which have less complicated radicles. In attempting this there are two side decompositions to be guarded against: First. The oxidation of dibenzoyl-methane to benzoic acid, etc. Second. The formation of *p*. sulphonic-aniline-sulphate. The well known method of Skraup (no oxidizing agent was added however) was first tried. Masses of white crystalline plates sublimed out which proved on examination to be benzoic acid, showing that the dibenzoyl-methane had been oxidized. Next, a mixture consisting of ten parts sulphuric acid and one part dibenzoyl-methane were heated to 100° and aniline added to the solution drop by drop. One hour was occupied in the addition. No condensation took place, for on pouring into ice water the entire quantity of dibenzoyl-methane separated out and no blue fluorescence was noticeable.

It was next tried heating one part dibenzoyl-methane, one part aniline and two parts aniline hydrochloride together in a sealed tube for several hours at a temperature of $200-240^{\circ}$. No condensation took place. The dibenzoyl-methane separated out nearly in the form of harz on treatment with hydrochloric acid.

The last attempt was, by heating the two in a closed tube with five parts concentrated hydrochloric acid into which hydrochloric acid gas had been led under cooling by a freezing mixture. After heating for a long time at a temperature of 180° no condensation had taken place and at a higher temperature decomposition resulted instead of condensation.

Bringing the results obtained by the various oxidations together we have the following table :

Quinoline - alkylen base	Under ice cooling to n-methyl-quinolon.
Quinaldine-alkylen base	Partially at the ordinary temperature, completely at a temperature of 30-40° to a red dye base. Unoxidized product.
α -Phenyl-quinoline-methyl hydroxide	Not oxidized at the ordinary temperature. Completely at a temperature of 30-40° to α -Phenyl-methyl-quinolon.
α - γ -Dimethyl-quinoline-methyl hydroxide	At the ordinary temperature to a blue dye base. More fully at a higher temperature. Unoxidized product.
γ -Phenyl-quinaldine-methyl hydroxide	At the ordinary temperature with formation of an unstable quinolon? To a red dye base at a higher temperature leaving unoxidized product.
Flavolinium-methyl hydroxide	No oxidation at the ordinary temperature. At 50-60° to a green dye base. Unoxidized product.

In the preceding table it will be noticed that when Quinaldine-alkylene base was subjected to oxidation—methyl group in α position—a color base resulted and that some unoxidized material was found in the solution on shaking out with ether.—This reaction was sharp owing to the absolute insolubility of the dye base in the latter reagent.—This shows that the color base obtained was not a simple partial oxidation product but was a more complex molecule (which is incapable of further oxidation) formed by the oxidation of the methyl group. The extent of this oxidation is not known but it undoubtedly prevents the formation of a quinolon.

One of the many Quinolons obtained by Decker was a nitro-p-methyl-n-methyl-quinolon,¹ This contains a methyl

¹ Jour. Pkt. Chem. 45 177.

group in the para position which was not oxidized under similar circumstances, and proves that the tendency to oxidize at definite points is what caused its oxidation and not its ready oxidizibility. When the more stable phenyl group occupied the α position oxidation still resulted with formation of α -Phenyl-methyl-quinolon proving oxidation had taken place at some other point. From previous work on the subject by Decker and other reactions on which Claus bases his benzene structural formula there is undoubtedly a close connection between groups attached to the carbon atoms in the para position to one another; therefore this point would undoubtedly be the γ carbon atom. That the oxidation took place at this point is proved by methyl-flavolinium hydroxide in which the phenyl group occupies the γ position and the methyl group the α . It will be noticed that a higher temperature ($50-60^{\circ}$) was necessary to produce its oxidation—also in the case of α -phenyl-quinolinium-methyl hydroxide $30-40^{\circ}$ —than was needed when the oxidation resulted in the α position.

That the oxidation of methyl-flavolinium hydroxide took place at the γ position and that the H or group occupying it is not as readily oxidized as if it occupied the α is proved by γ -phenyl-quinaldinium hydroxide. This is oxidized at the ordinary temperature and the entire oxidation must take place in the α radicle. This gives a determined grade to the ease with which the simple hydrogen atoms in groups occupying the α and γ positions are oxidized.

The apparent formation of an extremely unstable quinolon on the oxidation of γ -Phenyl-quinaldinium-methyl hydroxide is at present unexplainable as the privilege of seeing if the oxidation would be diverted to the β or some other position, if both the α and γ radicles were occupied by the more stable phenyl group, was not permitted owing to my failure to obtain α - γ -diphenyl-quinoline.

The fact that some of the ammonium hydroxides prepared were apparently soluble in absolute ether is regarded as a gradual change of form. The solutions of the ammonium hydroxides were very concentrated and were shaken out with much ether. That there is a tendency for the ammonium hydroxides to form anhydrides is stated by Claus in his article,

“Über die quaternären Ammonium basen.”¹ This is thought to be proved to be the case by the following observations:

First. No difference was observed between the residues left on evaporation of the ethereal solutions after treatment with sodium hydrate.

Second. On shaking the ethereal solution with water no alkaline reaction was imparted to the latter.

Third. The base was not all directly dissolved by the ether but vigorous shaking with much ether was necessary showing that the solubility was slight or rather dehydration slow.

It is to be noticed that the ammonium hydroxides which undergo this change have the methyl group in the α position, viz.: γ -Phenyl-quinaldinium-methyl hydroxide, α - γ -Dimethyl-quinolinium-methyl hydroxide, α - γ -Dimethyl-quinolinium-ethyl hydroxide—while those which have the phenyl group in the α position are not soluble in ether, viz.: α -Phenyl-quinolinium-methyl hydroxide² and Methyl-flavolinium hydroxide.

This stability is doubtless due in some way to the character of the substituting groups but exactly what this relation is cannot be determined at present.

The correctness of the constitutions assumed for the unstable bases—described in this paper—produced by the action of sodium hydrate on ammonium iodides, was questioned on noticing the results obtained in the case of Quinaldine-methyl hydroxide by Döbner & Möller.³ Their analysis corresponds with the formula $(C_9H_6CH_3NCH_3)_2O$ and not with the methylene base $C_9H_6CH_3NCH_2$ the theoretical limit of dehydration.

A similar compound has also been described by La Casta⁴ $(C_9H_6BrNCH_3)_2O$. This however has since been proven by Decker⁵ to have been the oxidation product, quinolon.

The result of the analyses following, at first sight would cause the conclusion to be drawn that the constitution given by

¹ Jour. Pkt. Chem. **46** 108.

² Büttner, Inaugural Dissertation, Freiburg i. B.

³ Ann. **243** 303.

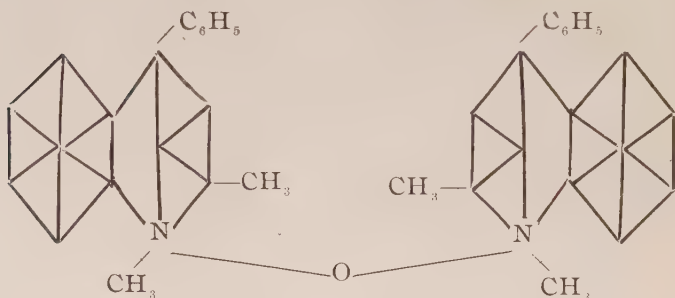
⁴ Ber. d. Chem. Ges. XV. 186.

⁵ Jour. Pkt. Chem. **45** 161.

Döbner & Möller for this class of compounds was correct, it is however not so regarded. There are instead a series of intermediate hydrates possible, which if more stable, could doubtless be dehydrated until the theoretical limit of dehydration—methlene base—of Claus was reached.

Owing to the affinity of these bases for oxygen the greatest care was necessary in handling them.

γ -Phenyl-methyl-quinaldinium-oxide



Several grams of γ -Phenyl-quinaldine-iodo-methylate in aqueous solution were placed in a separatory funnel, covered with a layer of ether and a dilute sodium hydrate solution added until no further oily precipitate separated. After shaking out with ether several times the extracts were dehydrated by standing one day in a corked flask—just large enough to hold it—containing a few pieces of solid caustic potash. It was then filtered quickly (scarcely necessary) into a carefully dried separatory funnel which was fitted into the neck of a small two-tubed distillation flask. One of the tubes was connected with a filter-pump, the other to a hydrogen generator. More ethereal solution was run into the flask when the first portion had evaporated, avoiding air contact. In this way the ether was quickly evaporated without the application of heat. A current of dry hydrogen gas was passed through the apparatus for some time after the ether had evaporated in order to remove its last traces. There remained in the flask a little, thin flowing, red-colored liquid. This was quickly sucked into a small pipet which was then sealed; taken to the weighing room; the liquid introduced into a tared weighing tube and immediately weighed for analysis. The analysis fol-

lowed as quickly as possible. It was made fresh for each determination.

Analysis :

I. Combustion.

0.1839 grms. substance gave 0.1024 grms. H_2O and
0.5671 grms. CO_2 .

Calculated for } 84.23% C. Found: 84.10% C.
formula given } 6.61% H. " 6.18% H.

II. Combustion.

0.1149 grms. substance gave 0.0715 grms. H_2O and
0.3567 grms. CO_2 .

Calculated : 84.23% C. Found: 84.59% C.
" 6.61% H. " 6.91% H.

I. Nitrogen determination.

0.1230 grms. substance gave 5.5 C.C. Nitrogen gas.

Barometer stand, 791. Temperature, 19° .

Calculated: 5.99% N. Found: 5.47% N.

II. Nitrogen determination.

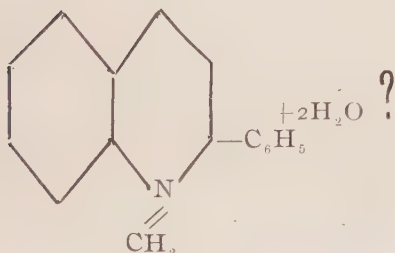
0.2030 grms. substance gave 9.4 C. C. Nitrogen gas.

Barometer stand, 772. Temperature, 15° .

Calculated: 5.99% N. Found: 5.60% N.

A drop of the thin flowing liquid on being placed on a watch glass soon became coated with a soft shiny skin by oxidation to a red dye derivative. It is nearly insoluble in water and very soluble in ether as previously stated.

α -Phenyl-methyl-quinolinium oxide.



On adding sodium hydrate to an aqueous solution of α -Phenyl-quinoline-iodo-methylate, as previously stated in this paper, there separates a yellow, oily precipitate, which on standing a few days becomes crystalline.

These crystals were found to have a melting point of $106-8^\circ$ or that of the corresponding oxidation product or quinolon.

It was made in large quantity and purified in exactly the same manner, with the same apparatus as described in the preceding compound. Owing to its greater stability however it was found possible to heat the brownish, yellowish syrupy liquid to a temperature of $60-70^{\circ}$ without decomposition; this was therefore done after the ether had volatilized and the dry hydrogen gas was being conducted through the apparatus.

Analysis :

I. Combustion.

0.3638 grms. substance gave 0.1989 grms. H_2O .

Found : 6.62% H.

II. Combustion.

0.1288 grms. substance gave 0.0786 grms. H_2O . and .3839 grms. CO_2 .

Found : 81.28% C. 6.70% H.

III. Combustion.

0.1374 grms. substance gave 0.0816 grms. H_2O . and 0.4097 grms. CO_2 .

Found : 81.29% C. 6.59% H.

The per cent. corresponds with $C_9H_6C_6H_5NCH_2 + 2H_2O$. The calculated per cent. for this being 81.31% C. and 5.93% H.

It is however thought that this composition is not definite being dependent entirely on the length of time heated and the degree of heat employed.

It was next endeavored to remove this molecule of water by further heating in a partial vacuum on a water bath. A slow current of dry hydrogen gas was conducted through the apparatus during the operation. Care must be exercised in regard to the heat and pressure at first on account of the violent boiling of the thick syrup. A small part distilled over into an ice-cooled receiver as a thick syrup. The remainder gradually grew darker. After three hours of this treatment the operation was interrupted. There remained in the flask a black, brittle residue which was stable in the air and melted at a temperature of about 60° . It was insoluble in water, but was completely dissolved on the addition of hydrochloric acid. It dissolves in ether (alcohol free) to a brownish-yellow solution, which on evaporation—cold, in vacuum—left a thick, brownish

syrup. This on analysis gave 80.03% C and 6.80% H. As it could not be recrystallized an analysis was made of the black residue. The result however was unsatisfactory it giving 85.78% C. and 6.40% H. The theoretical requirements for $C_{32}H_{28}N_2O$ are 81.21% C. and 6.14% H.; $C_{16}H_{13}N$, 87.63% C. 5.94% H. The result laying between that required for the oxide and methylene base.

With care it is possible to make the above without any quinolon (oxidation) being formed, but if oxidation takes place the latter can easily be removed by taking advantage of its slow solubility in ether. The hydrous base dissolves immediately, the anhydrous more slowly.

It was thought that the tendency of the arsonium hydroxides to form anhydrides observed by Eisenlohr¹ would add additional evidence to the preceding rather imperfectly substantiated theory in regard to the constitution of the quinoline bases—resulting by the action of sodium hydrate—of which the close examination—made in the well-appointed laboratories of Prof. Dr. A. Michaelis—just described, failed to give agreeing results. Eisenlohr found that m. tritolylyl-methyl-arsonium hydroxide $(CH_3C_6H_4)_3AsCH_3OH$ changed its character on standing—“Das zuerst erhaltene Tritolylyl-methyl-arsonium hydroxyd zeigt bei nur kurzem Stehen an der Luft ein eigentümliches verhalten. Die ölige Masse erstarrt Krystallinisch und wird in Wasser und verdünnter Salz saure auch beim Kochen vollständig unloslich. Aus Alkohol Krystalensiert die Substanz in glänzenden Blättchen vom Schmelzpunkt $96^\circ C$.”

The reaction which had taken place was supposed to be $2(CH_3C_6H_4)_3AsCH_3OH - H_2O = [(CH_3C_6H_4)_3AsCH_3]_2O$.

This however is not the case as shown by the following work with the homologous compound triphenyl-methyl-arsonium hydroxide (Gimborn²) $(C_6H_5)_3AsCH_3OH$, instead, decomposition into tertiary arsine and alcohol results.

$(CH_3C_6H_4)_3AsCH_3OH = (CH_3C_6H_4)_3As + CH_3OH$, in the same manner as that given for the corresponding aromatic

¹ Inaug. Dissertation, Rostock, 1893, p.

² Inaug. Dissertation, 1891, Rostock, p. 32.

ammonium hydroxides by Claus & Rautenberg.¹ They found that trimethyl-phenyl-ammonium hydroxide decomposed into dimethyl-aniline and methyl alcohol on distillation with sodium hydrate.



The mistake in regard to the result of this reaction was only detected in the present case through the failure to obtain agreeing melting points for the platinum double salts made from both the supposed oxide and hydroxide. This led to a closer investigation. The difference in the theoretical requirements for the constituent elements being less than one per cent. afforded insufficient evidence for the *detection of the error*.

As starting material it was necessary to prepare triphenyl-methyl-arsonium iodide. This was made according to the method described by Gimborn,² viz.: Triphenyl-arsine (Michaelis³) was dissolved in an excess of methyl-iodide and heated for several hours in a small flask with reflux condenser. The separated solid mass was, after the removal of methyl-iodide excess and the scarcely necessary treatment with ether, obtained in pure white crystal plates which had a melting point of 170–171°.

The arsonium-iodide, in aqueous solution, after treatment with the required quantity of moist silver oxide is completely converted into the ammonium hydroxide. Its solution on evaporation left an oily residue which after several days crystallized in white needles which were readily soluble in water. The arsonium hydroxide was heated on a water bath for 3–4 hours in an open dish. It was found that now only a portion was soluble in water even on heating and the addition of hydrochloric acid. The insoluble portion was found to be readily soluble in ether, from which solution it was obtained, on spontaneous evaporation, in well-formed clear crystal plates; these after recrystallization from alcohol were found to have a melting point of 58–59°, the same as that of triphenyl-arsine. It is also to be noticed that the melting point of m-Tritolyl-arsine is the same as that of the oxide described by Eisenlohr.

¹ Ber. d. Chem. Ges. XIV. 620.

² Inaug. Dissertation, Rostock, 1891, p. 31.

³ Ann. 201, 337.

This decomposition was found to take place quickly by boiling the arsonium hydroxide under reduced pressure, but did not result on allowing it to stand for one week in an evacuated dessicator containing solid caustic potash and sulphuric acid; it being still readily and entirely soluble in water.

A combustion gave the following result :

Analysis :

0.1455 grms. substance gave 0.0765 grms. H_2O and 0.3726 grms. CO_2 .

Found : 69.83% C and 5.83% H;

The theoretical requirements for Triphenyl-arsine $(C_6H_5)_3As$ are 70.58% C and 4.90% H. The percentage corresponds better with the requirements of the oxide $[(C_6H_5)_3AsCH_3]_2O$ however, they being 69.60% C and 5.47% H. That it must be triphenyl-arsine was further proved by forming the methyl-iodide from the triphenyl-arsine resulting by the decomposition—methyl-iodide could not thus be added if it were the oxide. No difference was to be observed in its addition or appearance and the melting point $172-3^\circ$ fully proved its identity.

The decomposition may be expressed by the following formula :



The Triphenyl-arsine resulting from the decomposition was brought into aqueous solution by first rubbing in a mortar with phosphorus pentachloride, also by conducting a stream of dry chlorine gas over it, doubtless with formation of the dichloride. It is practically insoluble in pure, concentrated hydrochloric acid even on protracted boiling.

There results a rather insoluble platinum double salt, on the introduction of platinic chloride into its solution, which closely resembles the platinum double salt resulting from triphenyl-arsonium-methyl hydroxide, both in stability, appearance and percentage of metallic platinum contained. The melting point however of the latter was found to be as given by Gimborn,¹ 225° ; that of the former, 211° . Although repeated efforts were made to obtain the same platinum double

¹ Inang. Dissertation, Rostock, 1891

salt from pure triphenyl-arsine handled in exactly the same manner as that resulting from the decomposition it was not accomplished. The platinum double salt from pure triphenyl-arsine (having exactly the same melting point as the supposed triphenyl-arsine resulting by the decomposition) melted at 175° even after repeated recrystallizations. The meaning of this difference and its explanation is necessary before the result of the preceding decomposition is fully cleared.

On account of the almost if not entirely proved fact that the arsonium hydroxides deport themselves like quaternary ammonium hydroxides—decomposing into alcohol and tertiary base—no evidence is produced which can be used in drawing conclusions in regard to the constitution of the quinolinium bases resulting by the action of sodium hydrate on the methyl-iodides. Owing to the differing results obtained with the two examples analyzed, one cannot but regard both as intermediate hydrates. The more stable of the two loses water with comparative ease, but the nature of the remaining brittle, black mass renders its purification impossible and owing to its impurity no definite result can be obtained; but the one given would seem to show that the methylene base of Prof. Dr. Claus was an undoubted reality, although its actual analysis in pure condition must be made by some future investigator.

The preceding Dissertation was worked out in the chemical laboratories of the Freiburg iB and Rostock iM Universities, with the assistance of Prof. Dr. Claus and Prof. Dr. Michaelis.

I take pleasure here in expressing my cordial and heartfelt thanks to my most respected teacher, Prof. Dr. A. Michaelis, for his kind assistance in the completion of this work.

